

REMARKS

Applicants have amended their specification in order to correct typographical and grammatical errors, including in light of objections to the disclosure on pages 2 and 3 of the Office Action mailed October 16, 2003; and to provide correct dimensions for the additive concentration in the sixth column of Table 1 on page 17 of Applicants' specification. See, for example, the description at page 13, lines 26-28 of Applicants' application, in connection with this additive concentration, it is respectfully submitted that the amendments to the specification do not add new matter to the application.

Applicants have amended their claims in order to further clarify the definition of various aspects of the present invention. In particular, Applicants have amended claim 3 to recite that the bath includes a solution containing copper ions, at least one of electrolytes, and at least one of the compounds represented by the general formula (I); and have incorporated the subject matter of claim 6 into claim 3. Similarly, claim 13 has been amended to recite that the bath includes a solution containing copper ions, at least one of electrolytes, and additives selected from a specified group thereof; and to incorporate the subject matter of claim 6 therein. In light of amendments to claims 3 and 13, Applicants have canceled claim 6 without prejudice or disclaimer. In addition, Applicants are amending claim 9 to recite that the at least one of the compounds of the general formula (I) is added at the recited concentration.

Moreover, Applicants are adding new claims 14-24 to the application. Claim 14 corresponds to claim 12, but is dependent on claim 13. Claims 15 and 16,

dependent respectively on claims 13 and 3, recite that the additives (or the at least one of the compounds represented by the general formula (I)) suppress the electroplating reaction during use of the copper electroplating bath and are consumed as the electroplating reaction proceeds, with a diffusion rate thereof being lower than a rate of reaction thereof during the use of the copper electroplating bath. Note, for example, pages 11 and 12 of Applicants' specification. Claims 17 and 18, dependent respectively on claims 3 and 17, respectively recites that at least one polyether is added to a copper electroplating bath, and further defines such at least one polyether; and claims 19 and 20, dependent respectively on claims 3 and 19, respectively recites that at least one organic sulfur compound is added to the copper electroplating bath, and further defines this at least one organic sulfur compound. See page 14 of Applicants' specification. Claims 21 and 22 recite subject matter as in claims 12 and 14, respectively, and further recite that the least one of the compounds represented by the general formula (I) (or the additives) suppresses the electroplating reaction and is consumed as the electroplating reaction proceeds, and has a diffusion rate lower than a rate of reaction thereof during the process. Claims 23 and 24, dependent respectively on claims 12 and 14, recite that concentration of the at least one of the compounds represented by the general formula (I) (or of said additives) in the electroplating bath, at the bottoms of the features, during the process, is less than that at a top of the features. See page 12 of Applicants' specification.

The election of species set forth on page 2 of the Office Action mailed October 16, 2003, is noted. Applicants are retaining non-elected claims in the

application, subject to a final determination in connection with generic claim 13. In this regard, it is noted that in the Amendment filed September 22, 2003, Applicants clearly alleged that claim 13 is a generic claim, and the Examiner has not traversed such allegation by Applicants. Again, upon allowance of claim 13, and upon amending various of the claims (e.g., claims 1 and 2) consistent with amendments to claims 3 and 13, it is respectfully submitted that all claims presently in the application should be allowed to issue in a single patent from the above-identified application.

It is respectfully submitted that, of the claims presently in the application, claims 3, 9 and 12-24 read on the elected species, and should be considered on the merits in the above-identified application.

Applicants respectfully traverse the rejection of claim 13 under the first paragraph of 35 U.S.C. §112, as set forth in Item I bridging pages 3 and 4 of the Office Action mailed October 16, 2003, especially insofar as this rejection is applicable to the claims as presently amended. Thus, claim 13 has now been amended to recite that the bath includes a solution containing, inter alia, copper ions, at least one of electrolytes, and additives selected from a specific group of at least one of cyanine dyes, at least one of indolium compounds and at least one of the compounds represented by the general formula (I). In view of the Markush group as now set forth in claim 13, it is respectfully submitted that claim 13 is proper, when defining the recited group, in utilizing the word "and" before the recitation of "at least one of the compounds represented by... general formula (I)". In view of the present amendments to claim 13, it is respectfully submitted that the rejection thereof under the first paragraph of 35 U.S.C. §112 is moot.

Applicants respectfully traverse the rejection of claims 3, 6, 9, 12 and 13 under the second paragraph of 35 U.S.C. §112, set forth in Item II bridging pages 4 and 5 of the Office Action mailed October 16, 2003, particularly insofar as this rejection is applicable to claims as presently amended. Thus, it is respectfully submitted that, as presently amended, claims 3 and 13 are clear with respect to the components of the solution of the copper electroplating bath. That is, this solution contains (1) copper ions, (2) at least one of electrolytes, and (3) at least one of the compounds represented by the general formula (I) (see claim 3) (or additives selected from a specific group thereof – see claim 13). That is, it is respectfully submitted that the claims are clear that the solution contains at least one of electrolytes and (i) at least one of the compounds represented by the general formula (I), as in claim 3, or and (ii) additives selected from the specified group thereof in claim 13.

The question by the Examiner on page 5 of the Office Action mailed October 16, 2003, as to whether the electrolytes are “addition compounds”, is noted. It is respectfully submitted that the claims as presently amended are clear that the solutions contain at least one of electrolytes as a component, with the additional component of at least one of the compounds represented by general formula (I) or the additives.

Applicants respectfully submit that all of the claims presented for consideration by the Examiner patentably distinguish over the teachings of the references applied by the Examiner in rejecting claims in the Office Action mailed October 16, 2003, that is, the teaching of the U.S. Patents to Barstad, et al.,

No. 6,444,110, and to Landau, No. 6,261,433, and the publication by Gerenrot, et al., "Effect of the Structure of Carbocyanine Dyes on the Leveling Power During the Electrodeposition of Copper", in Zashchita Metallov (1972), vol. 8, no. 3, pages 338-42, under the provisions of 35 U.S.C. §102 and 35 U.S.C. §103.

Initially, it is noted that the subject matter of claim 6 has been incorporated into each of claims 3 and 13. In view thereof, it is respectfully submitted that the claim rejections under 35 U.S.C. §102, set forth in Items 1 and 2 on pages 5-7 of the Office Action mailed October 16, 2003, are moot.

With respect to the remaining prior art rejections, it is respectfully submitted that the teachings of the applied prior art would have neither disclosed nor would have suggested such a copper electroplating bath, or such a method using such electroplating bath, as in the present claims, wherein the bath contains, in addition to copper ions and at least one of electrolytes, at least one of the compounds represented by the general formula (I), or additives selected from the group consisting of at least one of cyanine dyes, at least one of indolium compounds and at least one of the compounds represented by the general formula (I), with the bath also including one or more of polyethers, organic sulfur compounds and halide ions. See claim 3; note also claim 13.

In addition, it is respectfully submitted that these references as applied by the Examiner would have neither disclosed nor have suggested such copper electroplating bath as in the present claims, having features as discussed previously, and moreover wherein the at least one of the compounds of the general formula (I) is added in a concentration of 1-15 mg/L (see claim 9); and/or wherein at least one

polyether (see claims 17 and 18) or at least one organic sulfur compound (see claims 19 and 20) is included in the bath; and/or wherein the additives (or compounds represented by the general formula (I)) suppress the electroplating reaction during use of the copper electroplating bath and are consumed as the electroplating reaction proceeds, with a diffusion rate thereof being lower than a rate of reaction thereof during the use of the copper electroplating bath (see claims 15 and 16; note also claims 21 and 22); and/or wherein the concentration of the compounds represented by the general formula (I), or of the additives, in the electroplating bath, at the bottoms of the features, during the process, is less than that at the top of the features (see claims 23 and 24).

The present invention is directed to a copper plating bath, in particular a copper electroplating bath used for depositing copper in, and filling, fine openings or grooves in insulating layers, used, for example, in manufacturing semiconductor integrated circuit devices having multi-layer interconnections.

Recently, copper has been used for interconnections of large-scale integrated circuits, replacing aluminum and alloys thereof, due to, e.g., relatively low resistance of the copper. When using copper, it is difficult to pattern by dry etching, to form fine patterns, because copper does not produce a compound having a high vapor pressure. Accordingly, there has been employed a technique, called a Damascene technique, wherein trenches and vias are formed in insulating layers and filled with copper, the copper being isolated in the trenches and vias by, e.g., chemical mechanical polishing. While various techniques for filling the trenches and vias have been proposed, electroplating is the most promising as a method for filling the

trenches and vias. Note, for example, the paragraph bridging pages 2 and 3 of Applicants' specification.

While various techniques have been studied to fill trenches and vias with metals by electroplating, each of the proposed techniques has a problem, as discussed on pages 3 and 4 of Applicants' specification. These problems include, in particular, wherein voids and seams occur in the trenches and vias, particularly those having a high aspect ratio; and there is a particular need for a technique which allows such fine features to be completely filled.

Against this background, Applicants provide a technique wherein a completely filled feature (e.g., trench or via) can be provided, without generating voids and seams, even where such feature has a high aspect ratio; and, moreover, wherein uniformity in film thickness and film flatness are achieved. Applicants have found that by including in the copper electroplating bath, in addition to copper ions and at least one of electrolytes, at least one of the compounds represented by general formula (I) in claim 3 (or additives selected from the group consisting of at least one of cyanine dyes, at least one of indolium compounds, and at least one of the compounds represented by general formula (I)), objectives according the present invention are achieved. That is, the electroplated copper fills the inside of the feature, without voids or seams; and, moreover, the deposited structure has a uniform film thickness and film flatness on, e.g., the wafer upon which the copper is electrodeposited, facilitating polishing of the plated copper.

In connection with advantages achieved by the present invention, note, for example, Tables 1 and 2 respectively on pages 17 and 21 of Applicants'

specification. Note that Sample Numbers 1, 2 and 9 do not contain the additional additive selected from the group consisting of polyethers, organic sulfur compounds and halide ions, while Sample Numbers 3-8 contain such additional components. As can be seen, for example, in Table 2, uniformity is much better in connection with Sample Numbers 3-8. This evidence in Applicants' specification must be considered in determining unobviousness. See *In re DeBlauwe*, 222 USPQ 191 (CAFC 1984). This evidence further supports the conclusion of unobviousness of the presently claimed subject matter.

Gerenrot reports on the results of a study of the relation between the structure of polymethine dyes (carbocyanines, styryls) and their leveling power during Cu electrodeposition from acid solutions. This document discloses that the leveling additives used were carbocyanine dyes with symmetric and asymmetric structures containing quinoline, benzothiazole, indolenine and 5-phenyloxazole rings. The copper was electrodeposited on sectors of long-playing record matrixes from a specified solution, and leveling power was detected. The greatest leveling power was observed with carbocyanines with the highest basicity.

The Examiner has specifically pointed to No. 5 in the Table on page 339 of this article, with respect to compounds represented by the general formula (I).

It is respectfully submitted that Gerenrot discloses including a material providing increased leveling power; that is, that the material is adsorbed on convex portions of the plated material so as to hinder the plating reaction at locations where the electric field is concentrated, so that the rate of the plating reaction on concave portions is relatively high and the surface thereof is smooth. In contrast, the

additives (including the at least one compound having the general formula (I)) used according to present invention restrain a plating reaction at upper portions of the concave portions, and with progress of plating the restraining effect is decreased. That is, the amount of the additives diffused to concave portions is relatively small so that their concentration is lowered and its effect on restraining the plating reaction at concave portions is reduced. As a result, the rate of the plating reaction on the concave portions is relatively high, so that the concave portions can be filled up with a good efficiency. According to the present invention, use of the recited compounds forms a difference in the concentration thereof in the solution adjacent the bottom of the feature as compared to the concentration at other locations of the feature. Accordingly, concave portions can be filled with a good efficiency, even in the case of fine wiring.

In addition, according to the present invention the polyethers, organic sulfur compounds and/or halide ions are further added so as to easily control the effect of restraining the plating reaction at the top of the features as compared to at the bottom of the features, whereby fine vias and trenches (to form fine plugs and wirings having high aspect ratios) can be efficiently and effectively filled, without voids or seams, providing layers which have uniform thickness and have flatness.

Clearly, the disclosure of Gerenrot, et al., would not have disclosed or suggested the plating bath having specific components providing advantages according to the present invention, including filling concave portions efficiently and effectively, providing an electrodeposited film that is flat and has uniform thickness of the formed film.

It is respectfully submitted that not all the compounds disclosed in Gerenrot, et al., would achieve advantageous effects as in the present invention. It is respectfully submitted that Applicants have found specific groups of compounds, particularly together with the at least one of polyethers, organic sulfur compounds and halide ions as a further component of the copper electroplating bath, achieving advantages as discussed previously.

It is respectfully submitted that the secondary references as applied by the Examiner would not have rectified the deficiencies of Gerenrot, et al., such that the presently claimed invention as a whole would have been obvious to one of ordinary skill in the art.

Barstad, et al., discloses copper electroplating solutions, methods for using the solutions and products formed by using such methods and solutions, the solutions having increased brightener levels for effective plating of high aspect ratio apertures. See column 1, lines 7-14, and column 2, lines 55-57. Note also column 3, lines 41-46, disclosing that the compositions according to this patent suitably contain a copper salt, an electrolyte (preferably an acidic aqueous solution such as a sulfuric acid solution with a chloride or other halide ion source), and one or more brightener agents in enhanced concentrations, and preferably a suppressor agent. Note column 3, lines 41-46. See, further, the paragraph bridging columns 2 and 3, disclosing concentration of brightener in the plating solution. Note further column 5, lines 3-61, disclosing various useful brighteners; and column 6, lines 23-38, disclosing preferred suppressor agents.

Even assuming, arguendo, that the teachings of Barstad, et al., were properly

compatible with the teachings of Gerenrot, et al., such combined teachings would have neither disclosed nor would have suggested the copper electroplating bath or process of use thereof, as in the present claims, including the additives (inter alia, the at least one of the compounds represented by the general formula(I)) and the at least one of polyethers, organic sulfur compound and halide ions, and advantages thereof as discussed in the foregoing.

Contentions by the Examiner in connection with the teachings of Barstad, et al., in the first and second full paragraphs on page 8 of the Office Action mailed October 16, 2003, are noted. While discussing preferred suppressor agents, it is respectfully submitted that this patent does not disclose, nor would have suggested, additives and/or compounds represented by the general formula (I) as in the present claims. Furthermore, Barstadt, et al., discloses incorporation of increased amount of conventional brighteners for effective plating of high aspect ratio apertures. That is, it is respectfully submitted that this patent discloses increased amount of brighteners for the plating of high aspect ratio apertures. It is respectfully submitted that Barstad, et al., even in combination with the teachings of Gerenrot, et al., would have neither taught nor would have suggested the additives (including at least one of the compounds of the general formula (I)) and at least one of polyethers, organic sulfur compounds and halide ions, and advantages of this combination in the solution containing copper ions and at least one of electrolytes, as in the present invention; and, more particularly, would have neither disclosed nor would have suggested features of the present invention as set forth, for example, in claims 15, 16 and 21-24.

Landau discloses apparatus and a method for electroplating a metal layer onto a substrate, the apparatus being described most generally in the paragraph bridging columns 4 and 5 of this patent. As for the chemistry of the electrodeposition, note column 17, lines 41-44 and 57-59; and column 18, lines 12-15, of this patent. As for operating condition, see columns 15-17 of this patent.

Barstad, et al., and Gerenrot, et al., have been previously discussed.

Even assuming, arguendo, that the teachings of Barstad, et al., and Gerenrot, et al., were properly combinable with the teachings of Landau, such combined teachings would have neither disclosed nor would have suggested the presently claimed bath and process, including wherein the solution of the bath contains both the additive (e.g., at least one of the compounds represented by the general formula (I)) and the at least one of polyethers, organic sulfur compounds and halide ions, and advantages thereof, as discussed previously; and, more specifically, those further features of the components as in claims 15, 16 and 21-24.


In addition, with respect to the contention by the Examiner that Barstad, et al., discloses a plating bath containing a halide ion source, attention is respectfully directed to claims 17-20; it is respectfully submitted that the teachings of the applied prior art would have neither disclosed nor would have suggested these features of the present invention.

In view of the foregoing comments and amendments, reconsideration and allowance of all claims remaining in the application are respectfully requested.

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deposit account of Antonelli, Terry, Stout & Kraus, LLP, Deposit Account No. 01-2135 (referencing case no. 500.40269X00).

Respectfully submitted,



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